Study on Practical Synthesis of Symmetric/Unsymmetric Porphycenes and Their Complexes

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論 文 名　：Study on Practical Synthesis of Symmetric/Unsymmetric Porphycenes and Their Complexes
（対称/非対称ポルフィセンの実践的合成法の開拓とその錯体形成に関する研究）

区　　分　：甲

論 文 内 容 の 要 旨

The porphyrins and their complexes have been widely used in biological chemistry as well catalytic chemistry owing to their excellent photophysical and electrochemical properties. Moreover, it is known that a porphycene (**Pc**), a structural isomer of porphyrin, has been reported in 1986 by Vogel *et al.*, exhibiting more prominent optoelectronic functions with 18 π-conjugated aromatic character and lower symmetry structure (D_{2h}) as compared to that (D_{4h}) of porphyrins. Owing to the special characteristics, porphycenes, especially unsymmetric porphycenes, and their complexes have attracted considerable attention in photodynamic therapy (PDT), protein mimicry, catalysis, material science and some other areas. However, to date, the application of porphycenes is still very limited and only a few interesting results have been brought forth or just mentioned. Such a more slowly development of porphycene chemistry than that of porphyrin is mainly owing to the lack of efficient and economical methods for their production. Moreover, the small center cavity of porphycenes limit their coordinate ability with the element in the periodic table. To date, the coordination chemistry of metalloporphycenes with some common transition-metal elements has been obtained and studied, whereas the literature about the nonmetal-porphycene is rare. What's more, only few elements were successfully inserted into the porphycene which contains substituted groups in their *meso* positions. Therefore, in order to improve the situation of porphycene chemistry, in this thesis, a practical synthesis of symmetric/unsymmetric porphycenes and their complexes were investigated. The details of this work were described as below (**Figure 1**).

Chapter 2 *Meso*-tetraarylporphycenes were synthesized on the gram scale in a few steps with high overall yields, which are optimized by acid catalyzed oxidative reaction of *E/Z*-mixture of 5,6-diaryldipyrroethene followed by treatment with moderate oxidant such as chloranil. Moreover, the substituted groups on the *meso*-position can greatly affected the formation of porphycenes, especially, the yields of **FPc** and **CF_3Pc**, which contains electron-withdrawing groups, in oxidative coupling reactions by corresponding 5,6-diaryldipyrroethenes leads to 70% and 80%. What's more, the *E/Z*-isomerization of 5,6-diaryldipyrroethene under acidic condition is regarded as the key to proceed the effective macrocyclization, which are supported by both experimentally and theoretically.

Chapter 3 A series of AABB-, ABAB-, and ABBA-type unsymmetric porphycenes were successfully prepared with two different AA- and BB-dipyrroethenes, or AB-dipyrroethenes, as precursors in the yield up to 19% for the first time. These structures were unambiguously confirmed by X-ray crystallography. By comparation, the unsymmetric porphycenes showed medium values for the optical and electrochemical properties, implying the potential to tune the properties of porphycenes by change their substituents. Furthermore, the different electrochemical stabilities between AABB- and ABAB-unsymmetric porphycenes indicate that substituent positions also affected and finely tuned the properties of porphycenes.

Chapter 4 The first use of porphycene as ligand to yield boron complexes by microwave-assisted method was investigated. Two different coordination structure, mono- and diboron porphycene, were obtained at same time. The complexes were characterized by means of IR, UV-Vis, Emission, Quantum Yield, Lifetime, NMR, MALDI-TOF-MS, X-ray crystallography, DFT calculations as well as cyclic voltammetry. The result of single crystal structure and DFT calculation indicate that the boron coordinate site of mono-boron porphycenes were found on the unique dipyrroethene site and diboron porphycene preferentially exhibited a *cisoid* geometry. Moreover, unlike the fluorescence disappear phenomenon in the case of diboron porphycenes, the mono-boron complexes exhibited a red shift fluorescence compare to free base **Pc**. The electrochemical properties of porphycenes bring great changes after the insertion of boron atom, as a result, the boron complexes shows a more easily reduced redox properties. In addition, the protonation conducted for mono-boron porphycene which have one protonated site by addition of TFA was investigated for the first time, the resulting shows that both absorption and emission spectra performs a significantly red shift after protonated treatment.

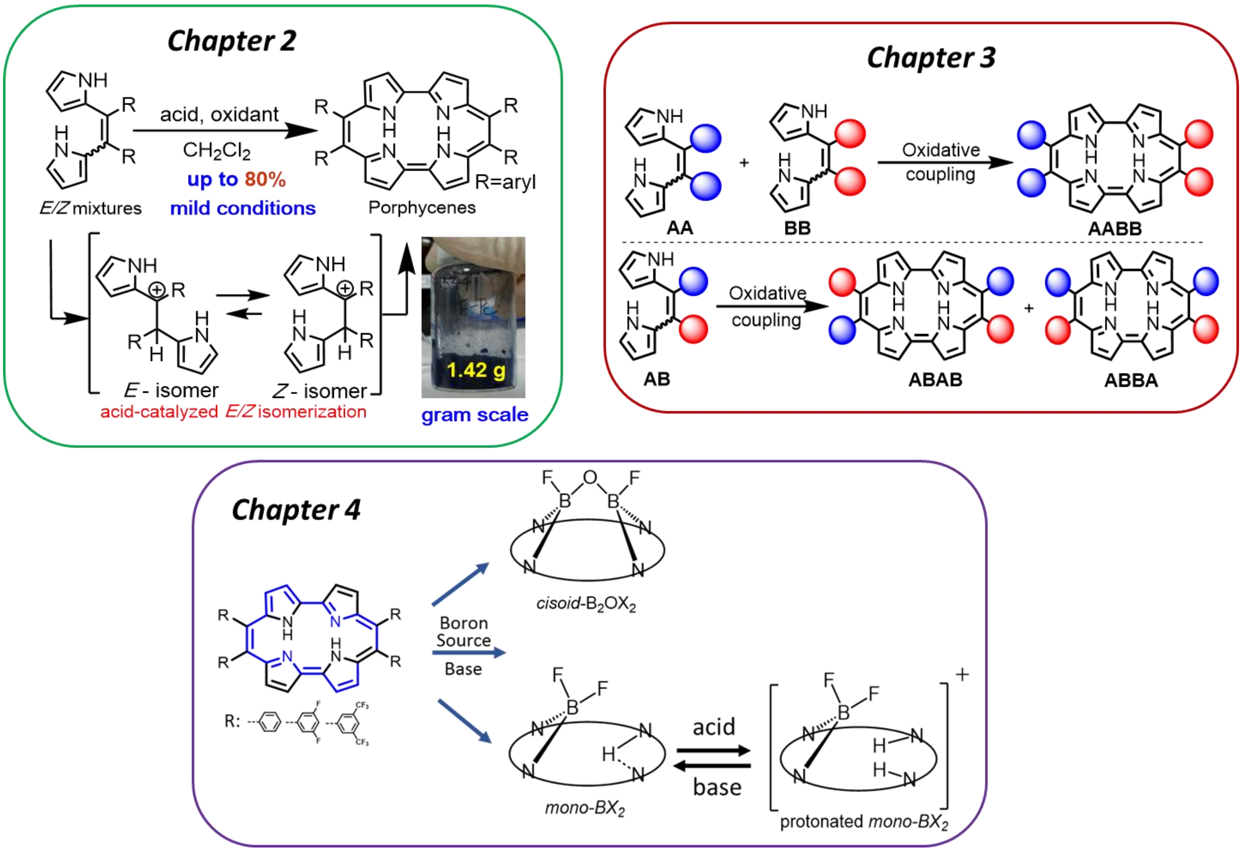

Figure 1. Synthetic Scheme of Chapter 2, 3, and 4.